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(54) DESULFURIZATION AGENT, METHOD OF DESULFURIZATION AND METHOD OF MANUFACTURING HYDROGEN FOR FUEL CELL

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a desulfurization agent capable of removing sulfur in a petroleum hydrocarbon oil and having a long service life, a method of desulfurization capable of removing sulfur in the petroleum hydrocarbon oil to a low concentration and a method of manufacturing hydrogen for a fuel cell.

SOLUTION: At least an element selected from the 17th group of elements on periodic table is carried on a carrier as the desulfurization agent for the petroleum hydrocarbon oil. The petroleum hydrocarbon oil is desulfurized by the desulfurization agent and, depending on the circumstances, by the method of desulfurization to be in contact with a second desulfurization agent. The petroleum hydrocarbon oil after contacting with the second desulfurization agent is in contact with a steam reforming catalyst, and then hydrogen for the fuel cell is manufactured.

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CLAIMS

[Claim(s)]

[Claim 1] The devulcanizing agent for petroleum system hydrocarbons which is chosen as support from the 17th group elements of the periodic table and which comes to support a kind at least.

[Claim 2] The devulcanizing agent for petroleum system hydrocarbons according to claim 1 whose petroleum system hydrocarbon is kerosene.

[Claim 3] The devulcanizing agent for petroleum system hydrocarbons according to claim 1 or 2 whose support is porosity.

[Claim 4] The devulcanizing agent for petroleum system hydrocarbons according to claim 1 to 3 whose support is the thing which is chosen from a silica, an alumina, a silica alumina, a zeolite, a titania, a zirconia, a magnesia, a zinc oxide, clay, clay, diatomaceous earth, and activated carbon, and which consists of a kind at least.

[Claim 5] The devulcanizing agent for petroleum system hydrocarbons according to claim 1 to 4 whose 17th group element of the periodic table is a bromine.

[Claim 6] The devulcanizing agent for petroleum system hydrocarbons according to claim 1 to 5 which is chosen as support from the 17th group elements of the periodic table and which makes it come 0.1 to 20% of the weight based on the devulcanizing-agent whole quantity at least to support a kind.

[Claim 7] The desulfurization approach of the petroleum system hydrocarbon characterized by using a devulcanizing agent according to claim 1 to 6.

[Claim 8] - The desulfurization approach of a petroleum system hydrocarbon according to claim 7 of contacting a petroleum system hydrocarbon to a devulcanizing agent in the temperature of 40-100 degrees C.

[Claim 9] The desulfurization approach of the petroleum system hydrocarbon characterized by making the second devulcanizing agent contact after carrying out desulfurization processing of the petroleum system hydrocarbon by the approach according to claim 7 or 8.

[Claim 10] The desulfurization approach of the petroleum system hydrocarbon according to claim 9 which is that in which the second devulcanizing agent contains at least a kind of metal chosen from Cr, Mn, Fe, Co, nickel, Cu, Zn, Pd, Ir, and Pt.

[Claim 11] The manufacture approach of the hydrogen for fuel cells characterized by making a steam-reforming catalyst contact after carrying out desulfurization processing of the petroleum system hydrocarbon by the approach according to claim 9 or 10.

[Claim 12] The manufacture approach of the hydrogen for fuel cells according to claim 11 that a steam-reforming catalyst is a ruthenium system catalyst.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a devulcanizing agent, the desulfurization approach, and the manufacture approach of the hydrogen for fuel cells. This invention removes the sulfur content in a petroleum system hydrocarbon for the sulfur content in a petroleum system hydrocarbon efficiently to low concentration removable using the long devulcanizing agent of a life, and this devulcanizing agent effectively, carries out steam-reforming processing of the desulfurization approach that long duration may be made to carry out rear-spring-supporter maintenance of the engine performance of the reforming catalyst in the steam-reforming part which is a down-stream facility, and the petroleum system hydrocarbon processed by this desulfurization approach, and relates to the approach of manufacture the hydrogen for fuel cells, in more detail.

[0002]

[Description of the Prior Art] In recent years, the new energy technique is in the limelight from the environmental problem, and the fuel cell attracts attention as one of the new energy technique of this. When this fuel cell makes hydrogen and oxygen react electrochemically, chemical energy is transformed into electrical energy, it has the description that the utilization effectiveness of energy is high, and utilization research is positively made as a noncommercial use, industrial use, or an object for automobiles. According to the class of electrolyte used for this fuel cell, the type of a phosphoric-acid mold, a melting carbonate mold, a solid acid ghost mold, a solid-state macromolecule mold, etc. is known. The activity of hydrocarbons, such as LPG of a petroleum system, naphtha, and kerosene, is studied by the town gas which, on the other hand, uses as a principal component the liquefied natural gas which makes a methanol and methane a subject, and this natural gas as a source of hydrogen, the synthetic liquid fuel which uses natural gas as a raw material, and the pan. When using a fuel cell for a noncommercial use or automobiles, since the distribution system is fixed, a gas station, a dealer, etc. are advantageous [the above-mentioned petroleum system hydrocarbon] as sources of hydrogen the top where storage and handling are easy. However, a petroleum system hydrocarbon has the problem that there are many contents of sulfur content, compared with the thing of a methanol or a natural gas system. When manufacturing hydrogen using this petroleum system hydrocarbon, generally steam reforming or the approach of carrying out partial oxidation refining processing is used for the bottom of existence of a reforming catalyst in this hydrocarbon. In such refining processing, in order to carry out poisoning of the above-mentioned reforming catalyst by the sulfur content in a hydrocarbon, it is important to perform desulfurization processing to this hydrocarbon and to usually make a sulfur content content below into the 0.2 weight ppm from the point of a catalyst life.

[0003] The approach which research of the former many is made, for example, is hydrodesulfurized at the temperature of 200-400 degrees C under the pressure of ordinary pressure -5MPa as the desulfurization approach of a petroleum system hydrocarbon using hydrogen-sulfide adsorbents, such as hydrodesulfurization catalysts, such as Co-Mo/alumina, and nickel-Mo/alumina, and ZnO, is learned. This approach performs hydrodesulfurization under

severe conditions, it is the approach of using sulfur content as a hydrogen sulfide and removing it, and since it is difficult, making sulfur content below into the 0.2 weight ppm moreover cannot apply it to the hydrocarbon for fuel cells easily. Activated carbon and a zeolite are known as matter which the approach physical adsorption removes some sulfur compounds is learned as the desulfurization approach of a petroleum fraction on the other hand (a U.S. Pat. No. 4188285 description, JP,3-128989,A, JP,6-154615,A, a U.S. Pat. No. 5482617 description, a U.S. Pat. No. 5807475 description, International Patent Publication No. 98151762, U.S. Pat. No. 5935422 description), and is used for clearance. Furthermore, the method of contacting further the petroleum fraction which removed some sulfur compounds by physical adsorption to a devulcanizing agent is also learned (a U.S. Pat. No. 5114689 description, Patent Publication Heisei No. 504214 [seven to] official report). However, activated carbon and a zeolite have the low adsorption engine performance to a sulfur compound, and the actual condition is that the physical-adsorption agent used in the above-mentioned approach has not resulted in practical level in respect of a life as a devulcanizing agent for fuel cells.

[0004]

[Problem(s) to be Solved by the Invention] The 1st object of this invention is under such a situation to be able to remove the sulfur content in a petroleum system hydrocarbon effectively, and offer the long devulcanizing agent of a life. Moreover, using this devulcanizing agent, the 2nd object of this invention removes the sulfur content in a petroleum system hydrocarbon efficiently to low concentration, and is to offer the desulfurization approach that long duration may be made to carry out rear-spring-supporter maintenance of the engine performance of the reforming catalyst in the steam-reforming part which is a down-stream facility. Furthermore, the 3rd object of this invention is to offer the approach of manufacturing the hydrogen for fuel cells efficiently, using the petroleum system hydrocarbon processed by the above-mentioned desulfurization approach.

[0005]

[Means for Solving the Problem] In order that this invention persons might attain said object, as for the sulfur compound which analyzes in a detail and is contained in a petroleum system hydrocarbon, benzothiophene or dibenzo thiophenes solved the dominant thing in the desulfurization engine performance about the description of the sulfur compound in a petroleum system hydrocarbon first. Then, in order to have removed effectively the benzothiophene which is hard to be desulfurized among the sulfur compound in a petroleum system hydrocarbon, i.e., a mercaptan, a thiophene, a sulfide, disulfide, benzothiophene, and dibenzo thiophenes, and dibenzo thiophenes, reactant and a petroleum system hydrocarbon were strongly contacted to the sulfur of benzothiophene and dibenzo thiophenes, and it noted that what is necessary was just to carry out adsorption treatment of the resultant containing sulfur. That this invention persons should develop the sulfur of benzothiophene and dibenzo thiophenes, and the devulcanizing agent which contains reactant strongly based on this view As a result of repeating research wholeheartedly, the thing which comes to support the 17th group element of the periodic table to support, especially porosity support It could react with benzothiophene and dibenzo thiophenes, adsorption treatment of the sulfur could be carried out selectively, and it found out that said 1st object might be suited as a devulcanizing agent for petroleum system hydrocarbons. Moreover, it found out that said 2nd object could be attained by carrying out desulfurization processing of the petroleum system hydrocarbon, and making the second devulcanizing agent contact by the case further using the above-mentioned devulcanizing agent.

[0006] Furthermore, in the above-mentioned desulfurization approach, it found out that said 3rd object could be attained by contacting the petroleum system hydrocarbon after making the second devulcanizing agent contact for a steam-reforming catalyst. This invention is completed based on this knowledge. Namely, the devulcanizing agent for petroleum system hydrocarbons by which this invention is chosen as (1) support from the 17th group elements of the periodic table and which comes to support a kind at least, (2) The desulfurization approach of the petroleum system hydrocarbon characterized by using the above-mentioned devulcanizing agent, (3) After carrying out desulfurization processing of the petroleum system hydrocarbon by the approach of the above (2), After carrying out desulfurization processing of the petroleum system hydrocarbon

by the desulfurization approach of the petroleum system hydrocarbon characterized by making the second devulcanizing agent contact, and the approach of (4) above (3), the manufacture approach of the hydrogen for fuel cells characterized by making a steam-reforming catalyst contact is offered.

[0007]

[Embodiment of the Invention] First, the devulcanizing agent of this invention is explained. The devulcanizing agent of this invention makes a kind support that it is few as being chosen as support from the 17th group elements of the periodic table, and its bromine is desirable especially as the 17th group element of the periodic table. This bromine reacts with sulfur and changes to a sulfur bromide with the adsorption capacity force higher than benzothiophene and dibenzo thiophenes. In this invention, a hydride is suitable as description of this 17th group element of the periodic table. Moreover, the approach of carrying out direct gas adsorption of the hydride, or carrying out impregnation of the water solution of this hydride as an approach of making support supporting this 17th group element, is used preferably. When a bromine is used as the 17th group element, a porous body is adsorbed easily and the sulfur bromide generated at the reaction can reduce the sulfur content concentration in a petroleum system hydrocarbon.

[0008] The amount of support of the 17th group element of the periodic table to support has 0.1

– 20% of the weight of the desirable range based on the devulcanizing-agent whole quantity. If there is a possibility that the desulfurization engine performance may not fully be demonstrated for this amount at less than 0.1 % of the weight and it, on the other hand, exceeds 20 % of the weight, this 17th group element may be eluted in a hydrocarbon, and it is not desirable. From such a reason, the more desirable amount of support is 0.1 – 10% of the weight of the range. In this invention, a porous thing is desirable as support. As such porosity support, a porosity inorganic oxide, for example, a silica, an alumina, a silica alumina, a zeolite, a titania, a zirconia, a magnesia, a zinc oxide, clay, clay, diatomaceous earth, etc. can be mentioned preferably, and activated carbon can also be used. Although such porosity support may be used independently and may be used combining two or more sorts, especially in these, activated carbon is suitable for it. Moreover, the condition of there being especially no limit as a configuration of a devulcanizing agent, for example, having coated other honeycomb-like base materials with the shape of the letter of grinding, a pellet type, and a tablet, the shape of a honeycomb, and devulcanizing-agent powder etc. can be mentioned. As a petroleum system hydrocarbon with which the devulcanizing agent of this invention is applied, although LPG, a gasoline, naphtha, kerosene, gas oil, etc. are mentioned, for example, kerosene is desirable in these. If it is in the petroleum system hydrocarbon which has the boiling point below kerosene, it is desirable that a sulfur content content applies to the JIS No. 1 kerosene below the 80 weight ppm.

[0009] Next, the desulfurization approach of this invention is explained. After carrying out desulfurization processing of the petroleum system hydrocarbon using the devulcanizing agent of this invention of (1) above-mentioned by the approach (the desulfurization approach I of this invention is called hereafter.) of carrying out desulfurization processing of the petroleum system hydrocarbon, and the (2) above-mentioned desulfurization approach I, there are two modes of an approach (the desulfurization approach II of this invention is called hereafter.) contacted to the second devulcanizing agent in the desulfurization approach of this invention. In the desulfurization approach I of this invention, a petroleum system hydrocarbon can be put into containers, such as an approach of circulating a petroleum system hydrocarbon to a devulcanizing agent, and a tank which fixed the devulcanizing agent to the interior, as a desulfurization format, and standing or the approach of agitating can be mentioned preferably. Moreover, the temperature to which this devulcanizing agent and a petroleum system hydrocarbon are contacted in this case has the desirable range of –40–100 degrees C. Since the adsorption engine performance of a devulcanizing agent will fall if this temperature exceeds 100 degrees C preferably, since the fluidity of this hydrocarbon falls below –40 degrees C, it is not desirable. In addition, a pressure is usually ordinary pressure –1MPa in this case.

[0010] In the desulfurization approach II of this invention, after being the above [a petroleum system hydrocarbon], making, using the devulcanizing agent of above-mentioned this invention as a reserve devulcanizing agent and carrying out desulfurization processing, adsorption

desulfurization of this hydrocarbon can be efficiently performed by using the second devulcanizing agent contact. This is because adsorption treatment of the difficulty desulfurization nature sulfur compound is carried out selectively by using the devulcanizing agent of this invention as a reserve devulcanizing agent. As the second devulcanizing agent of the above, there is especially no limit, it may use another adsorption devulcanizing agent, and may use hydrodesulfurization catalysts, such as Co-Mo/alumina, and Ni-Mo/alumina. As another former adsorption devulcanizing agent, the thing which is chosen, for example from Cr, Mn, Fe, Co, nickel, Cu, Zn, Pd, Ir, and Pt and which supported a kind to porosity support is desirable at least. What supported especially nickel to porosity support is suitable. As for the amount of support of these metal components, it is desirable that it is 40 - 80 % of the weight based on points, such as desulfurization engine performance, to the devulcanizing-agent whole quantity. These adsorption devulcanizing agents can raise the desulfurization engine performance by carrying out hydrogen reduction beforehand. Moreover, in using the latter hydrodesulfurization catalyst, in case it contacts a petroleum system hydrocarbon for this hydrodesulfurization catalyst as the second devulcanizing agent, a small amount of hydrogen may be added.

[0011] It is desirable to contact directly the petroleum system hydrocarbon in which desulfurization processing was carried out by the devulcanizing agent of this invention to the second devulcanizing agent as the desulfurization approach by this second devulcanizing agent. Moreover, beforehand, desulfurization processing is carried out by the devulcanizing agent of this invention, and a petroleum system hydrocarbon may be contacted to the second devulcanizing agent in somewhere else at reaction time. As a reaction condition at the time of making the second devulcanizing agent contact, a petroleum system hydrocarbon can be suitably selected according to the class of the second devulcanizing agent to be used. For example, when a nickel system adsorption devulcanizing agent is used as the second devulcanizing agent and kerosene is used as a petroleum system hydrocarbon, the range of contact temperature is usually 130-230 degrees C, and a pressure is usually ordinary pressure - 1 MPa-G extent. In the desulfurization approach II of such this invention, it is possible by choosing desulfurization conditions suitably to make sulfur content in a petroleum system hydrocarbon below into the 0.2 weight ppm.

[0012] Next, the manufacture approach of the hydrogen for fuel cells of this invention is explained. In this approach, the hydrogen for fuel cells is manufactured by contacting the petroleum system hydrocarbon by which desulfurization processing was carried out in the desulfurization approach II of said this invention for a steam-reforming catalyst. As a steam-reforming catalyst used in the approach of this invention, there is especially no limit, out of the well-known thing conventionally known as a steam-reforming catalyst of a hydrocarbon, can choose the thing of arbitration suitably and can use it. As such a steam-reforming catalyst, what supported noble metals, such as nickel, a zirconium or a ruthenium, a rhodium, and platinum, can be mentioned, for example to suitable support. Kind support may be carried out and the above-mentioned support metal may be made to support combining two or more sorts. In these catalysts, the thing (a ruthenium system catalyst is called hereafter.) which made the ruthenium support is desirable, and the effectiveness which controls the carbon deposit under steam-reforming reaction is large.

[0013] In the case of this ruthenium system catalyst, the amount of support of a ruthenium has 0.05 - 20% of the weight of the desirable range on support criteria, and it is 0.1 - 2% of the weight of the range especially preferably 0.05 to 15% of the weight more preferably. When supporting this ruthenium, it can support by request combining other metals. As these other metals, a zirconium, cobalt, magnesium, etc. are mentioned, for example. On the other hand, as support, an inorganic oxide is desirable and an alumina, a silica, a zirconia, magnesias, such mixture, etc. are specifically mentioned. In these, especially an alumina and a zirconia are suitable. a ratio with the carbon which originates in a steam and a petroleum system hydrocarbon as a reaction condition in steam-reforming processing -- S/C (mole ratio) -- usually -- 2-5 -- desirable -- 2-4 -- it is more preferably selected in 2-3. When there is a possibility that the amount of generation of hydrogen may fall [a S/C mole ratio] less than by two and 5 is exceeded, a superfluous steam is needed, a heat loss is large, and since the effectiveness of hydrogen manufacture falls, it is not desirable.

[0014] Moreover, it is desirable to keep the inlet temperature of a steam-reforming catalyst bed at 630 degrees C or less and 600 more degrees C or less, and to perform steam reforming. If inlet temperature exceeds 630 degrees C, the pyrolysis of a hydrocarbon may be promoted, carbon may deposit in a catalyst or a reaction tube wall, and operation may become difficult. In addition, although especially a limit does not have catalyst bed outlet temperature, the range of 650-800 degrees C is desirable. If catalyst bed outlet temperature has fear which is not enough and exceeds 800 degrees C, a reactor may need heat-resisting material and is not economically desirable. reaction pressure — usually — ordinary pressure — 3MPa — desirable — the range of ordinary pressure — 1MPa — it is — moreover, LHSV — usually — 0.1-100h⁻¹ — it is the range of 0.2-50h⁻¹ preferably. Thus, the hydrogen for fuel cells can be manufactured efficiently.

[0015]

[Example] Next, although an example explains this invention to a detail further, this invention is not limited at all by these examples. In addition, the kerosene used for the desulfurization trial is the JIS No. 1 kerosene of the sulfur content 65 weight ppm.

After mixing 50ml of hydrogen bromide water solutions of the 0.1 mols [1.] preparation concentration of an example 1 (1) devulcanizing agent, and 100g (specific surface area of 1000m² / g, pore volume of 0.98ml/g) of commercial activated carbon and agitating at a room temperature for 1 hour, it dried at 70 degrees C and the devulcanizing agent which consists of bromine support activated carbon was prepared. The amount of bromine support in this devulcanizing agent was 1 % of the weight.

(2) After holding 50g of devulcanizing agents and 200ml of JIS No. 1 kerosene obtained by the desulfurization test above (1) in glassware with a capacity of 500ml and agitating it at a room temperature for 24 hours, separation recovery of the part for kerosene was carried out. The sulfur content concentration in the collected kerosene was the 10 weight ppm.

[0016] In the preparation example 1 (1) of an example 2 (1) devulcanizing agent, the devulcanizing agent which consists of a bromine support Y mold zeolite was prepared like the example 1 (1) except having used Y mold zeolite (Si/aluminum mole ratio 34) instead of activated carbon. The amount of bromine support in this devulcanizing agent was 0.5 % of the weight.

(2) When the desulfurization trial was carried out like the example 1 (2) using the devulcanizing agent obtained by the desulfurization test above (1), the sulfur content concentration in the kerosene after recovery was the 15 weight ppm.

In the preparation example 1 (1) of the example 1 (1) devulcanizing agent of a comparison, the devulcanizing agent which consists of non-supported activated carbon was prepared like the example 1 (1) except having not used a hydrogen bromide water solution.

(2) When the desulfurization trial was carried out like the example 1 (2) using the devulcanizing agent obtained by the desulfurization test above (1), the sulfur content concentration in the kerosene after recovery was the 50 weight ppm.

[0017] In the preparation example 2 (1) of the example 2 (1) devulcanizing agent of a comparison, the devulcanizing agent which consists of a non-supported Y mold zeolite was prepared like the example 2 (1) except having not used a hydrogen bromide water solution.

(2) When the desulfurization trial was carried out like the example 2 (2) using the devulcanizing agent obtained by the desulfurization test above (1), the sulfur content concentration in the kerosene after recovery was the 53 weight ppm.

500g of devulcanizing agents and 2l. of JIS No. 1 kerosene prepared in the example 3(1) preliminary desulfurization processing example 1 were held in the container with a capacity of 5l., and after agitating for 24 hours and carrying out preliminary desulfurization processing at a room temperature, separation recovery of the part for kerosene was carried out. The sulfur content concentration in preliminary desulfurization processing kerosene was the 10 weight ppm.

(2) As the second devulcanizing agent of desulfurization processing by the nickel support diatomaceous earth devulcanizing agent, after calcinating 15ml (54.3 % of the weight the amount of nickel support : as metal nickel) of nickel support diatomaceous earth at 400 degrees C, the coil made from stainless steel with a bore of 17mm was filled up. Subsequently, after carrying out temperature up to 120 degrees C in the bottom hydrogen air current of ordinary pressure and holding for 1 hour, temperature up was carried out further, it held at 380 degrees C for 1 hour,

and the nickel support dia...aceous earth devulcanizing agent was...vated. Then, it held at 150 degrees C. Next, the above-mentioned preliminary desulfurization processing kerosene was circulated to the coil in liquid-hourly-space-velocity (LHSV) 5h-1 under ordinary pressure, and the sulfur content concentration in the processing kerosene after 5-hour progress was analyzed. Consequently, sulfur content concentration was the 0.4 weight ppm.

[0018] In example 4 example 2, except having set liquid hourly space velocity (LHSV) to 2h-1, similarly, the coil was passed and the refining machine filled up with 15 cc (the amount of Ru support: 0.5 % of the weight) of ruthenium system reforming catalysts performed steam-reforming processing on the lower stream of a river further. Refining conditions were 750 degrees C in pressure:ordinary pressure, the steam / carbon (S/C) mole ratio 2.5, LHSV2h-1, 500 degrees C of inlet temperatures, and outlet temperature. Consequently, the invert ratio in the refining machine outlet after 750-hour progress was 100%. Moreover, the sulfur content of the desulfurization processing kerosene in this period was below the 0.2 weight ppm. In (2), it carried out like the example 3 (2) except having used new JIS No. 1 kerosene instead of preliminary desulfurization processing kerosene, without performing (1) in example of comparison 3 example 3. Consequently, the sulfur content concentration in processing kerosene was the 2.3 weight ppm.

[0019] In (2), JIS No. 1 kerosene was diluted with Deccan which does not contain sulfur instead of preliminary desulfurization processing kerosene, without performing (1) in example of comparison 4 example 3, and it carried out like the example 3 (2) except having used what made sulfur content concentration the 10 weight ppm. Consequently, the sulfur content concentration in processing liquid was the 1.7 weight ppm. As mentioned above, from an example 3 and the examples 3 and 4 of a comparison, the devulcanizing agent of this invention shows that the sulfur content concentration of the kerosene in contact with the second devulcanizing agent is decreasing, as a result of carrying out adsorption treatment of some sulfur compounds in kerosene.

Steam-reforming processing was performed like the example 4 except having used the kerosene of the sulfur content 10 weight ppm prepared by the same approach as the example 4 of example of comparison 5 comparison. Consequently, the invert ratio was less than 100% after 520-hour progress. The sulfur content of the desulfurization processing kerosene at that time was 4 ppm.

[0020]

[Effect of the Invention] Its life is long while the devulcanizing agent of this invention comes to support the 17th group element of the periodic table to support and can remove effectively the sulfur content in a petroleum system hydrocarbon, especially kerosene. Moreover, according to the desulfurization approach of this invention, the sulfur content in a petroleum system hydrocarbon can be efficiently removed to low concentration, and a long time can be made to carry out rear-spring-supporter maintenance of the engine performance of the reforming catalyst in the steam-reforming part which is a down-stream facility. Moreover, the hydrogen for fuel cells can be efficiently manufactured by carrying out steam-reforming processing of the petroleum system hydrocarbon processed by this desulfurization approach.

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TECHNICAL FIELD

[Field of the Invention] This invention relates to a devulcanizing agent, the desulfurization approach, and the manufacture approach of the hydrogen for fuel cells. This invention removes the sulfur content in a petroleum system hydrocarbon for the sulfur content in a petroleum system hydrocarbon efficiently to low concentration removable using the long devulcanizing agent of a life, and this devulcanizing agent effectively, carries out steam-reforming processing of the desulfurization approach that long duration may be made to carry out rear-spring-supporter maintenance of the engine performance of the reforming catalyst in the steam-reforming part which is a down-stream facility, and the petroleum system hydrocarbon processed by this desulfurization approach, and relates to the approach of manufacture the hydrogen for fuel cells, in more detail.

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PRIOR ART

[Description of the Prior Art] In recent years, the new energy technique is in the limelight from the environmental problem, and the fuel cell attracts attention as one of the new energy technique of this. When this fuel cell makes hydrogen and oxygen react electrochemically, chemical energy is transformed into electrical energy, it has the description that the utilization effectiveness of energy is high, and utilization research is positively made as a noncommercial use, industrial use, or an object for automobiles. According to the class of electrolyte used for this fuel cell, the type of a phosphoric-acid mold, a melting carbonate mold, a solid acid ghost mold, a solid-state macromolecule mold, etc. is known. The activity of hydrocarbons, such as LPG of a petroleum system, naphtha, and kerosene, is studied by the town gas which, on the other hand, uses as a principal component the liquefied natural gas which makes a methanol and methane a subject, and this natural gas as a source of hydrogen, the synthetic liquid fuel which uses natural gas as a raw material, and the pan. When using a fuel cell for a noncommercial use or automobiles, since the distribution system is fixed, a gas station, a dealer, etc. are advantageous [the above-mentioned petroleum system hydrocarbon] as sources of hydrogen the top where storage and handling are easy. However, a petroleum system hydrocarbon has the problem that there are many contents of sulfur content, compared with the thing of a methanol or a natural gas system. When manufacturing hydrogen using this petroleum system hydrocarbon, generally steam reforming or the approach of carrying out partial oxidation refining processing is used for the bottom of existence of a reforming catalyst in this hydrocarbon. In such refining processing, in order to carry out poisoning of the above-mentioned reforming catalyst by the sulfur content in a hydrocarbon, it is important to perform desulfurization processing to this hydrocarbon and to usually make a sulfur content content below into the 0.2 weight ppm from the point of a catalyst life.

[0003] The approach which research of the former many is made, for example, is hydrodesulfurized at the temperature of 200-400 degrees C under the pressure of ordinary pressure -5MPa as the desulfurization approach of a petroleum system hydrocarbon using hydrogen-sulfide adsorbents, such as hydrodesulfurization catalysts, such as Co-Mo/alumina, and nickel-Mo/alumina, and ZnO, is learned. This approach performs hydrodesulfurization under severe conditions, it is the approach of using sulfur content as a hydrogen sulfide and removing it, and since it is difficult, making sulfur content below into the 0.2 weight ppm moreover cannot apply it to the hydrocarbon for fuel cells easily. Activated carbon and a zeolite are known as matter which the approach physical adsorption removes some sulfur compounds is learned as the desulfurization approach of a petroleum fraction on the other hand (a U.S. Pat. No. 4188285 description, JP,3-128989,A, JP,6-154615,A, a U.S. Pat. No. 5482617 description, a U.S. Pat. No. 5807475 description, International Patent Publication No. 98151762, U.S. Pat. No. 5935422 description), and is used for clearance. Furthermore, the method of contacting further the petroleum fraction which removed some sulfur compounds by physical adsorption to a devulcanizing agent is also learned (a U.S. Pat. No. 5114689 description, Patent Publication Heisei No. 504214 [seven to] official report). However, activated carbon and a zeolite have the low adsorption engine performance to a sulfur compound, and the actual condition is that the physical-adsorption agent used in the above-mentioned approach has not resulted in practical

level in respect of a life as a vulcanizing agent for fuel cells.

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EFFECT OF THE INVENTION

[Effect of the Invention] Its life is long while the devulcanizing agent of this invention comes to support the 17th group element of the periodic table to support and can remove effectively the sulfur content in a petroleum system hydrocarbon, especially kerosene. Moreover, according to the desulfurization approach of this invention, the sulfur content in a petroleum system hydrocarbon can be efficiently removed to low concentration, and a long time can be made to carry out rear-spring-supporter maintenance of the engine performance of the reforming catalyst in the steam-reforming part which is a down-stream facility. Moreover, the hydrogen for fuel cells can be efficiently manufactured by carrying out steam-reforming processing of the petroleum system hydrocarbon processed by this desulfurization approach.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] The 1st object of this invention is under such a situation to be able to remove the sulfur content in a petroleum system hydrocarbon effectively, and offer the long devulcanizing agent of a life. Moreover, using this devulcanizing agent, the 2nd object of this invention removes the sulfur content in a petroleum system hydrocarbon efficiently to low concentration, and is to offer the desulfurization approach that long duration may be made to carry out rear-spring-supporter maintenance of the engine performance of the reforming catalyst in the steam-reforming part which is a down-stream facility. Furthermore, the 3rd object of this invention is to offer the approach of manufacturing the hydrogen for fuel cells efficiently, using the petroleum system hydrocarbon processed by the above-mentioned desulfurization approach.

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MEANS

[Means for Solving the Problem] In order that this invention persons might attain said object, as for the sulfur compound which analyzes in a detail and is contained in a petroleum system hydrocarbon, benzothiophene or dibenzo thiophenes solved the dominant thing in the desulfurization engine performance about the description of the sulfur compound in a petroleum system hydrocarbon first. Then, in order to have removed effectively the benzothiophene which is hard to be desulfurized among the sulfur compound in a petroleum system hydrocarbon, i.e., a mercaptan, a thiophene, a sulfide, disulfide, benzothiophene, and dibenzo thiophenes, and dibenzo thiophenes, reactant and a petroleum system hydrocarbon were strongly contacted to the sulfur of benzothiophene and dibenzo thiophenes, and it noted that what is necessary was just to carry out adsorption treatment of the resultant containing sulfur. That this invention persons should develop the sulfur of benzothiophene and dibenzo thiophenes, and the devulcanizing agent which contains reactant strongly based on this view As a result of repeating research wholeheartedly, the thing which comes to support the 17th group element of the periodic table to support, especially porosity support It could react with benzothiophene and dibenzo thiophenes, adsorption treatment of the sulfur could be carried out selectively, and it found out that said 1st object might be suited as a devulcanizing agent for petroleum system hydrocarbons. Moreover, it found out that said 2nd object could be attained by carrying out desulfurization processing of the petroleum system hydrocarbon, and making the second devulcanizing agent contact by the case further using the above-mentioned devulcanizing agent.

[0006] Furthermore, in the above-mentioned desulfurization approach, it found out that said 3rd object could be attained by contacting the petroleum system hydrocarbon after making the second devulcanizing agent contact for a steam-reforming catalyst. This invention is completed based on this knowledge. Namely, the devulcanizing agent for petroleum system hydrocarbons by which this invention is chosen as (1) support from the 17th group elements of the periodic table and which comes to support a kind at least, (2) The desulfurization approach of the petroleum system hydrocarbon characterized by using the above-mentioned devulcanizing agent, (3) After carrying out desulfurization processing of the petroleum system hydrocarbon by the approach of the above (2), After carrying out desulfurization processing of the petroleum system hydrocarbon by the desulfurization approach of the petroleum system hydrocarbon characterized by making the second devulcanizing agent contact, and the approach of (4) above (3), the manufacture approach of the hydrogen for fuel cells characterized by making a steam-reforming catalyst contact is offered.

[0007]

[Embodiment of the Invention] First, the devulcanizing agent of this invention is explained. The devulcanizing agent of this invention makes a kind support that it is few as being chosen as support from the 17th group elements of the periodic table, and its bromine is desirable especially as the 17th group element of the periodic table. This bromine reacts with sulfur and changes to a sulfur bromide with the adsorption capacity force higher than benzothiophene and dibenzo thiophenes. In this invention, a hydride is suitable as description of this 17th group element of the periodic table. Moreover, the approach of carrying out direct gas adsorption of the hydride, or carrying out impregnation of the water solution of this hydride as an approach of

making support supporting 17th group element, is used preferably when a bromine is used as the 17th group element, a porous body is adsorbed easily and the sulfur bromide generated at the reaction can reduce the sulfur content concentration in a petroleum system hydrocarbon.

[0008] The amount of support of the 17th group element of the periodic table to support has 0.1 - 20% of the weight of the desirable range based on the desulfurizing-agent whole quantity. If there is a possibility that the desulfurization engine performance may not fully be demonstrated for this amount at less than 0.1 % of the weight and it, on the other hand, exceeds 20 % of the weight, this 17th group element may be eluted in a hydrocarbon, and it is not desirable. From such a reason, the more desirable amount of support is 0.1 - 10% of the weight of the range. In this invention, a porous thing is desirable as support. As such porosity support, a porosity inorganic oxide, for example, a silica, an alumina, a silica alumina, a zeolite, a titania, a zirconia, a magnesia, a zinc oxide, clay, clay, diatomaceous earth, etc. can be mentioned preferably, and activated carbon can also be used. Although such porosity support may be used independently and may be used combining two or more sorts, especially in these, activated carbon is suitable for it. Moreover, the condition of there being especially no limit as a configuration of a desulfurizing agent, for example, having coated other honeycomb-like base materials with the shape of the letter of grinding, a pellet type, and a tablet, the shape of a honeycomb, and desulfurizing-agent powder etc. can be mentioned. As a petroleum system hydrocarbon with which the desulfurizing agent of this invention is applied, although LPG, a gasoline, naphtha, kerosene, gas oil, etc. are mentioned, for example, kerosene is desirable in these. If it is in the petroleum system hydrocarbon which has the boiling point below kerosene, it is desirable that a sulfur content content applies to the JIS No. 1 kerosene below the 80 weight ppm.

[0009] Next, the desulfurization approach of this invention is explained. After carrying out desulfurization processing of the petroleum system hydrocarbon using the desulfurizing agent of this invention of (1) above-mentioned by the approach (the desulfurization approach I of this invention is called hereafter.) of carrying out desulfurization processing of the petroleum system hydrocarbon, and the (2) above-mentioned desulfurization approach I, there are two modes of an approach (the desulfurization approach II of this invention is called hereafter.) contacted to the second desulfurizing agent in the desulfurization approach of this invention. In the desulfurization approach I of this invention, a petroleum system hydrocarbon can be put into containers, such as an approach of circulating a petroleum system hydrocarbon to a desulfurizing agent, and a tank which fixed the desulfurizing agent to the interior, as a desulfurization format, and standing or the approach of agitating can be mentioned preferably. Moreover, the temperature to which this desulfurizing agent and a petroleum system hydrocarbon are contacted in this case has the desirable range of -40-100 degrees C. Since the adsorption engine performance of a desulfurizing agent will fall if this temperature exceeds 100 degrees C preferably, since the fluidity of this hydrocarbon falls below -40 degrees C, it is not desirable. In addition, a pressure is usually ordinary pressure -1MPa in this case.

[0010] In the desulfurization approach II of this invention, after being the above [a petroleum system hydrocarbon], making, using the desulfurizing agent of above-mentioned this invention as a reserve desulfurizing agent and carrying out desulfurization processing, adsorption desulfurization of this hydrocarbon can be efficiently performed by making the second desulfurizing agent contact. This is because adsorption treatment of the difficulty desulfurization nature sulfur compound is carried out selectively by using the desulfurizing agent of this invention as a reserve desulfurizing agent. As the second desulfurizing agent of the above, there is especially no limit, it may use another adsorption desulfurizing agent, and may use hydrodesulfurization catalysts, such as Co-Mo/alumina, and Ni-Mo/alumina. As another former adsorption desulfurizing agent, the thing which is chosen, for example from Cr, Mn, Fe, Co, nickel, Cu, Zn, Pd, Ir, and Pt and which supported a kind to porosity support is desirable at least. What supported especially nickel to porosity support is suitable. As for the amount of support of these metal components, it is desirable that it is 40 - 80 % of the weight based on points, such as desulfurization engine performance, to the desulfurizing-agent whole quantity. These adsorption desulfurizing agents can raise the desulfurization engine performance by carrying out hydrogen reduction beforehand. Moreover, in using the latter hydrodesulfurization

catalyst, in case it contains a petroleum system hydrocarbon for the hydrodesulfurization catalyst as the second devulcanizing agent, a small amount of hydrogen may be added.

[0011] It is desirable to contact directly the petroleum system hydrocarbon in which desulfurization processing was carried out by the devulcanizing agent of this invention to the second devulcanizing agent as the desulfurization approach by this second devulcanizing agent. Moreover, beforehand, desulfurization processing is carried out by the devulcanizing agent of this invention, and a petroleum system hydrocarbon may be contacted to the second devulcanizing agent in somewhere else at reaction time. As a reaction condition at the time of making the second devulcanizing agent contact, a petroleum system hydrocarbon can be suitably selected according to the class of the second devulcanizing agent to be used. For example, when a nickel system adsorption devulcanizing agent is used as the second devulcanizing agent and kerosene is used as a petroleum system hydrocarbon, the range of contact temperature is usually 130–230 degrees C, and a pressure is usually ordinary pressure – 1 MPa–G extent. In the desulfurization approach II of such this invention, it is possible by choosing desulfurization conditions suitably to make sulfur content in a petroleum system hydrocarbon below into the 0.2 weight ppm.

[0012] Next, the manufacture approach of the hydrogen for fuel cells of this invention is explained. In this approach, the hydrogen for fuel cells is manufactured by contacting the petroleum system hydrocarbon by which desulfurization processing was carried out in the desulfurization approach II of said this invention for a steam-reforming catalyst. As a steam-reforming catalyst used in the approach of this invention, there is especially no limit, out of the well-known thing conventionally known as a steam-reforming catalyst of a hydrocarbon, can choose the thing of arbitration suitably and can use it. As such a steam-reforming catalyst, what supported noble metals, such as nickel, a zirconium or a ruthenium, a rhodium, and platinum, can be mentioned, for example to suitable support. Kind support may be carried out and the above-mentioned support metal may be made to support combining two or more sorts. In these catalysts, the thing (a ruthenium system catalyst is called hereafter.) which made the ruthenium support is desirable, and the effectiveness which controls the carbon deposit under steam-reforming reaction is large.

[0013] In the case of this ruthenium system catalyst, the amount of support of a ruthenium has 0.05 – 20% of the weight of the desirable range on support criteria, and it is 0.1 – 2% of the weight of the range especially preferably 0.05 to 15% of the weight more preferably. When supporting this ruthenium, it can support by request combining other metals. As these other metals, a zirconium, cobalt, magnesium, etc. are mentioned, for example. On the other hand, as support, an inorganic oxide is desirable and an alumina, a silica, a zirconia, magnesias, such mixture, etc. are specifically mentioned. In these, especially an alumina and a zirconia are suitable. a ratio with the carbon which originates in a steam and a petroleum system hydrocarbon as a reaction condition in steam-reforming processing -- S/C (mole ratio) -- usually -- 2–5 -- desirable -- 2–4 -- it is more preferably selected in 2–3. When there is a possibility that the amount of generation of hydrogen may fall [a S/C mole ratio] less than by two and 5 is exceeded, a superfluous steam is needed, a heat loss is large, and since the effectiveness of hydrogen manufacture falls, it is not desirable.

[0014] Moreover, it is desirable to keep the inlet temperature of a steam-reforming catalyst bed at 630 degrees C or less and 600 more degrees C, and to perform steam reforming. If inlet temperature exceeds 630 degrees C, the pyrolysis of a hydrocarbon may be promoted, carbon may deposit in a catalyst or a reaction tube wall, and operation may become difficult. In addition, although especially a limit does not have catalyst bed outlet temperature, the range of 650–800 degrees C is desirable. If catalyst bed outlet temperature has fear which is not enough and exceeds 800 degrees C, a reactor may need heat-resisting material and is not economically desirable. reaction pressure -- usually -- ordinary pressure –3MPa -- desirable -- the range of ordinary pressure –1MPa -- it is -- moreover, LHSV -- usually -- 0.1–100h⁻¹ -- it is the range of 0.2–50h⁻¹ preferably. Thus, the hydrogen for fuel cells can be manufactured efficiently.

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EXAMPLE

[Example] Next, although an example explains this invention to a detail further, this invention is not limited at all by these examples. In addition, the kerosene used for the desulfurization trial is the JIS No. 1 kerosene of the sulfur content 65 weight ppm.

After mixing 50ml of hydrogen bromide water solutions of the 0.1 mols [/l.] preparation concentration of an example 1 (1) devulcanizing agent, and 100g (specific surface area of 1000m² / g, pore volume of 0.98ml/g) of commercial activated carbon and agitating at a room temperature for 1 hour, it dried at 70 degrees C and the devulcanizing agent which consists of bromine support activated carbon was prepared. The amount of bromine support in this devulcanizing agent was 1 % of the weight.

(2) After holding 50g of devulcanizing agents and 200ml of JIS No. 1 kerosene obtained by the desulfurization test above (1) in glassware with a capacity of 500ml and agitating it at a room temperature for 24 hours, separation recovery of the part for kerosene was carried out. The sulfur content concentration in the collected kerosene was the 10 weight ppm.

[0016] In the preparation example 1 (1) of an example 2 (1) devulcanizing agent, the devulcanizing agent which consists of a bromine support Y mold zeolite was prepared like the example 1 (1) except having used Y mold zeolite (Si/aluminum mole ratio 34) instead of activated carbon. The amount of bromine support in this devulcanizing agent was 0.5 % of the weight.

(2) When the desulfurization trial was carried out like the example 1 (2) using the devulcanizing agent obtained by the desulfurization test above (1), the sulfur content concentration in the kerosene after recovery was the 15 weight ppm.

In the preparation example 1 (1) of the example 1 (1) devulcanizing agent of a comparison, the devulcanizing agent which consists of non-supported activated carbon was prepared like the example 1 (1) except having not used a hydrogen bromide water solution.

(2) When the desulfurization trial was carried out like the example 1 (2) using the devulcanizing agent obtained by the desulfurization test above (1), the sulfur content concentration in the kerosene after recovery was the 50 weight ppm.

[0017] In the preparation example 2 (1) of the example 2 (1) devulcanizing agent of a comparison, the devulcanizing agent which consists of a non-supported Y mold zeolite was prepared like the example 2 (1) except having not used a hydrogen bromide water solution.

(2) When the desulfurization trial was carried out like the example 2 (2) using the devulcanizing agent obtained by the desulfurization test above (1), the sulfur content concentration in the kerosene after recovery was the 53 weight ppm.

500g of devulcanizing agents and 2l. of JIS No. 1 kerosene prepared in the example 3(1) preliminary desulfurization processing example 1 were held in the container with a capacity of 5l., and after agitating for 24 hours and carrying out preliminary desulfurization processing at a room temperature, separation recovery of the part for kerosene was carried out. The sulfur content concentration in preliminary desulfurization processing kerosene was the 10 weight ppm.

(2) As the second devulcanizing agent of desulfurization processing by the nickel support diatomaceous earth devulcanizing agent, after calcinating 15ml (54.3 % of the weight the amount of nickel support : as metal nickel) of nickel support diatomaceous earth at 400 degrees C, the coil made from stainless steel with a bore of 17mm was filled up. Subsequently, after carrying out

temperature up to 120 degrees C in the bottom hydrogen air current at ordinary pressure and holding for 1 hour, temperature up was carried out further, it held at 300 degrees C for 1 hour, and the nickel support diatomaceous earth devulcanizing agent was activated. Then, it held at 150 degrees C. Next, the above-mentioned preliminary desulfurization processing kerosene was circulated to the coil in liquid-hourly-space-velocity (LHSV) 5h⁻¹ under ordinary pressure, and the sulfur content concentration in the processing kerosene after 5-hour progress was analyzed. Consequently, sulfur content concentration was the 0.4 weight ppm.

[0018] In example 4 example 2, except having set liquid hourly space velocity (LHSV) to 2h⁻¹, similarly, the coil was passed and the refining machine filled up with 15 cc (the amount of Ru support: 0.5 % of the weight) of ruthenium system reforming catalysts performed steam-reforming processing on the lower stream of a river further. Refining conditions were 750 degrees C in pressure:ordinary pressure, the steam / carbon (S/C) mole ratio 2.5, LHSV2h⁻¹, 500 degrees C of inlet temperatures, and outlet temperature. Consequently, the invert ratio in the refining machine outlet after 750-hour progress was 100%. Moreover, the sulfur content of the desulfurization processing kerosene in this period was below the 0.2 weight ppm.

In (2), it carried out like the example 3 (2) except having used new JIS No. 1 kerosene instead of preliminary desulfurization processing kerosene, without performing (1) in example of comparison 3 example 3. Consequently, the sulfur content concentration in processing kerosene was the 2.3 weight ppm.

[0019] In (2), JIS No. 1 kerosene was diluted with Deccan which does not contain sulfur instead of preliminary desulfurization processing kerosene, without performing (1) in example of comparison 4 example 3, and it carried out like the example 3 (2) except having used what made sulfur content concentration the 10 weight ppm. Consequently, the sulfur content concentration in processing liquid was the 1.7 weight ppm. As mentioned above, from an example 3 and the examples 3 and 4 of a comparison, the devulcanizing agent of this invention shows that the sulfur content concentration of the kerosene in contact with the second devulcanizing agent is decreasing, as a result of carrying out adsorption treatment of some sulfur compounds in kerosene.

Steam-reforming processing was performed like the example 4 except having used the kerosene of the sulfur content 10 weight ppm prepared by the same approach as the example 4 of example of comparison 5 comparison. Consequently, the invert ratio was less than 100% after 520-hour progress. The sulfur content of the desulfurization processing kerosene at that time was 4 ppm.

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